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Impurities and Additives May Complicate Site Characterization

Stephen P. Vonder Haar, Robert A. Ferry and Thomas R. Berry • Weiss Associates • Emeryville, CA
Albert L. Lamarre • Lawrence Livermore National Laboratory • Livermore, CA

Several thousand analyses of groundwater, soil and rock, and soil gases have been performed to define the extent and fate of subsurface environmental contamination at Lawrence Livermore National Laboratory (LLNL) Site 300. The primary contaminant is trichloroethylene (TCE), which is currently used as a heat exchange fluid and has been used in the past as a general solvent; 45 other volatile organic compounds (VOCs) have been detected at lower concentrations. A literature review indicates that 71 chemicals may be present in commercial and reagent grade TCE as impurities and stabilizers; these may comprise 2 percent of the total weight. These data suggest that some VOCs detected at Site 300 and at other Superfund sites may be from TCE additives and impurities and do not represent independent chemical releases. If so, this would affect risk assessments, chemical "fingerprinting," and biodegradation calculations.

In 1955, LLNL Site 300 was established as a Department of Energy High-Explosives (HE) test facility. This 30-km^2 site is located in the rugged, semi-arid Altamont Hills southwest of Tracy, California. In 1983, environmental investigations began at Site 300; in 1990, Site 300 was placed on the National Priorities List (Superfund). Remedial Investigation/Feasibility Study (RI/FS) work is being conducted under CERCLA in six separate study areas at Site 300 (Figure 1) to investigate and remediate VOCs, HE, and/or tritium contamination in soil and groundwater.

These investigations have identified contaminant releases from firing tables, disposal pits, HE process areas, experimental facilities, and machine shops. More than 600 boreholes have been drilled, with 450 completed as groundwater monitor wells. More than 7,000 groundwater samples; 4,000 soil samples; and 900 soil vapor samples have been collected and analyzed. Investigations also included hydraulic tests, borehole geophysical logs, seismic reflection profiles, ground-penetrating radar and magnetic surveys, biotic assays, and analysis of aerial photographs. This paper describes the results of a literature search (Table 1) that confirms that TCE, which was and in some cases is still widely used in commercial and research applications, is not "pure." Rather, it may contain numerous impurities and additives, many of which are listed by the U.S. Environmental Protection Agency (EPA) as priority pollutants.

TCE (C_2HCl_3) was first prepared by Fischer in 1864. It has no known natural source. Before 1969, most of the production of TCE in the U.S. was from acetylene, but since then the bulk of TCE has been derived from ethylene or dichloroethane. In 1970, U.S. production reached 277 million kg; in 1973, worldwide production was 700 million kg. Production has decreased in recent years due to restrictions on emissions, the use of alternative solvents, and recycling. [1, 8] Worldwide, TCE has about 50 trade names.

TCE is primarily used as an industrial solvent in vapor degreasing and cold-cleaning of fabricated metal parts. It is also used in textile dry cleaning, solvent extraction processing of foods, adhesive and paint-stripping formulations, and many other applications. [1, 2, 8, 10] TCE is one of the most prevalent priority pollutant chemicals in soil and water in the U.S., and is particularly common in microelectronics areas such as the "Silicon Valley" in California. [7, 9] At LLNL Site 300, TCE is used as a heat exchange fluid for thermal testing of weapons components and has been used as a general solvent.

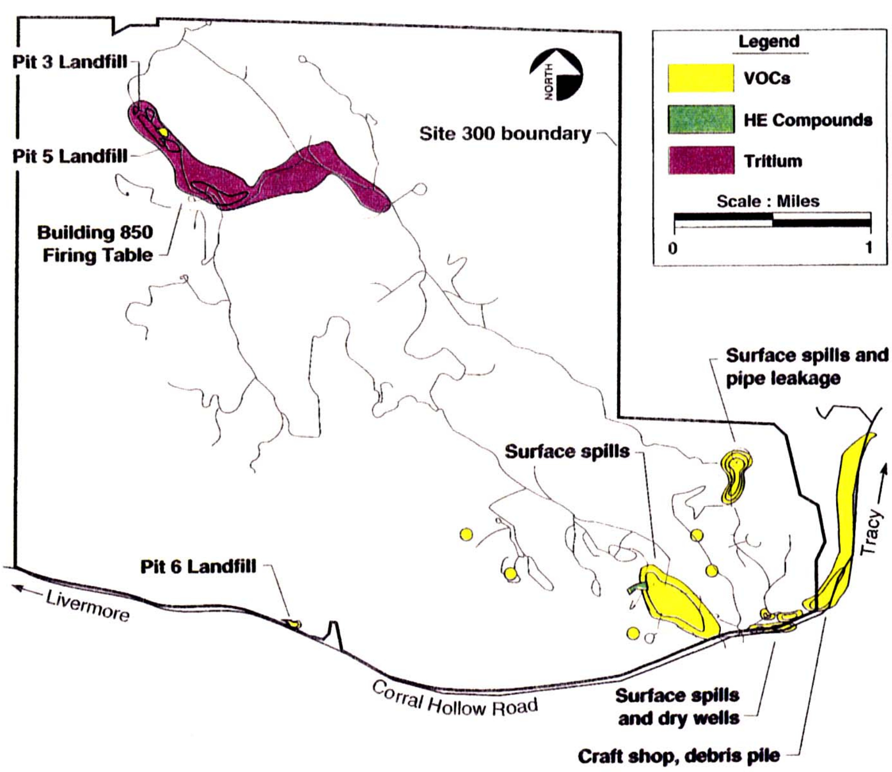

Figure 1 - Release points and extent of contaminants in groundwater at Lawrence Livermore National Laboratory Site 300.

The degree of TCE purity can vary; many commercial grades are about 98 percent pure, and reagent grades have a minimum purity of 99.85 percent. Commercial grades require stabilizers (up to 2 percent) in the form of acid-receptors or antioxidants. [2] Sample purity grades are identified by many names worldwide, including: analytical, technical, reagent, extraction, pharmaceutical, commercial anesthetic, pure, extra pure, vapor-degreasing, high purity, stabilized, low stabilized, regular, and paint application. [1, 3, 6, 8, 11]

It is uncommon for an individual impurity in TCE to be present in excess of 100 mg/kg (100 parts per million [ppm]), or for the total impurities to be greater than 1,000 mg/kg (1,000 ppm). [2, 5] However, the EPA Maximum Contaminant Levels (MCLs) for priority pollutants in drinking water are often in the part per billion (ppb) range—four or more orders of magnitude lower than the concentration of impurities in TCE. For example, tetrachloroethylene (PCE), carbon tetrachloride, and benzene, which are reported impurities in TCE, have U.S. EPA MCLs of 5 ppb. All three of these chemicals have been reported in the soil and groundwater at LLNL Site 300, along with TCE.

In addition to impurities comprised of organic compounds, TCE can contain trace

Table 1 - Chemicals Reported as TCE Impurities or Additives

acetone[a]	benzene[a]
1,1,1-trichloroethane (1,1,1-TCA) [a]	1,1,2-trichloroethane [a]
1,1,2,2-tetrachloroethane [a]	tetrahydrofuran [a]
1,2-dichloroethane (1,2-DCA) [a]	phenol[a]
perchloroethylene (PCE) [a]	methyl ethyl ketone (MEK)[a]
1,1,1,2-tetrachloroethane	carbon tetrachloride[a]
chloroform [a]	vinyl chloride
bromodichloroethylene	pentachloroethane
trans-1,2-dichloroethylene (trans-1,2-DCE) [a]	n-pentane
cis-1,2-dichloroethylene (cis-1,2-DCE) [a]	
1,1-dichloroethylene (1,1-DCE) [a]	
numerous stabilizers [b, c] such as:	
epichlorohydrin	1,2-epoxybutene
1,4-dioxane	propanol
2,2,4-trimethylpentene-1	propane
thymol	pentanol-2 triethanolamine
n-methylpyrrole	isocyanates
styrene oxide	cyclohexene oxide
diisopropylamine	hydrochloric acid
butylene oxide	ethyl acetate
diisobutylene	
38 *other chemicals* including esters, ketones, hydrocarbons, amines, cyclic ethers, and epoxides.	

[a] Chemicals also detected in LLNL Site 300 groundwater or soil.
[b] Stabilizers and impurities have been reported in TCE as typically comprising 0.5–2 percent by weight, up to 10 percent (5).
[c] LLNL Site 300 samples were not generally analyzed for these compounds; we focused on VOCs detected by EPA GC and MS Methods 601, 624, 8010, and 8240.

concentrations of metals, [4] some of which are regulated or carcinogenic toxins. For example, one batch of TCE used in carcinogenic studies [5] contained 26 ppm by weight of non-volatile and non-filterable residue. This residue was 990 ppm copper, 380 ppm zinc, 38 ppm chromium, 39 ppm strontium, 31 ppm lead, 1.4 ppm nickel, 1.3 ppm cobalt, and contained various concentrations of bismuth, cerium, lanthanum, barium, iodine, yttrium, bromine, manganese, titanium, aluminum, fluorine, boron, and lithium. If TCE such as this were spilled at Site 300 or at another hazardous waste site in the near-surface soil and rock, then some metal contamination could result due to the impurities in the TCE after the spilled TCE had volatilized.

Although this article focuses on TCE, impurities are common in other ordinary solvents. For example, 1,1,1-trichloroethane, a common industrial solvent, is often only 90 percent pure, and PCE may contain up to 1,000 ppm of 1,1,1-trichloroethane. [11] In a groundwater sample having 200 mg/L (ppm) of PCE, as much as 200 µg/L (ppb) of 1,1,1-TCA may be present as impurities, which equals the MCL for 1,1,1-TCA of 200 µg/L (ppb).

When conducting site background research (review of inventories, manifests, material purchases, etc.) it can be very useful to note specific chemical product information such as product names or grades used. In some cases, chemical product manufacturer data such as Material Safety Data Sheets will identify specific impurities present in the product.

Studies of degradation and transformation pathways for TCE and other volatile organic priority pollutants in the soil-groundwater system, [12] especially field studies such as those conducted at LLNL Site 300, may be complicated by the presence of impurities in the parent solvent (e.g., TCE). For example, it may be impossible in some cases to distinguish how much 1,2-DCE from a bioremediation test or from soil venting remediation was a result of degradation, as opposed to being an original constituent of the TCE. In addition, litigation and regulatory orders that attempt to use chemical "fingerprinting" (a suite of chemicals unique to a particular company, for example) to define liability at Superfund sites, often rely on trace VOC analyses. Such analyses for TCE and other VOCs that have impurities and stabilizers may hinder this technique.

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